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**Diesel Fuel  
Mini-processor**

**Phase I Report**

**Report to the  
Defense Advanced  
Research Projects Agency  
and to the  
US Army Research Office**

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## 1.0 Executive Summary

ADL contracted to DARPA and ARO to develop a diesel fuel processor for a 250W PEMFC based on ADL's miniPOX reformer. That miniPOX reactor has operated only with methanol, natural gas and propane; but never with diesel fuel, due to the soot that heavy hydrocarbons tend to produce when reformed. Phase I of this development was devoted to establishing the chemistry of pre-processing diesel fuel so that it would generate little or no soot in the miniPOX.

First, we established that our intended approach to pre-processing was impractical. This approach included the hydration of olefins, which process requires high pressures and separation/recirculation of the product stream.

Next, we established through chemical kinetics modeling that diesel fuel could be rendered no more soot-prone than gasoline by removing diesel fuel's polyaromatic compounds (PACs) and by cracking its naphthenes and olefins.

We then fabricated and tested a device that was intended to separate diesel fuel into light and heavy fractions, with the heavy fraction containing most or all of the PACs and naphthenes. The heavy fraction was vaporized and passed through a bed of coking catalyst, intended to crack these heavy fractions into light species suitable for POXing and heavy species to be sequestered as coke in the catalyst bed.

We observed, however, that the single plate still used to separate diesel fuel into heavy and light fractions was ineffective at this separation. A distillation column could provide adequate separation, but would be inappropriate to a small, portable application.

We observed also that the coker produced, in addition to light species and coke, a collection of heavy species not suitable for POXing. These species could readily be separated from the light species by condensation; again, this was felt to be inappropriate to a small, portable application.

We fed the product of this device to a small POX reactor and attempted to measure the soot in the POX exhaust. We were unable to do so with the three techniques we attempted, though we feel that one technique (scattering of a laser beam) could be developed to work.

We then qualitatively analyzed the insulation requirements of a small POX reactor that must maintain the high temperature necessary to prevent it from forming tar when fed diesel fuel, pre-processed or not. We determined that there is a minimum firing rate for POX reactors, which may very well be larger than is called for by this application.

We recommend that the concept of pre-processing diesel fuel be further explored in the context of larger, stationary systems; that the minimum practical size of POX reactors be determined both experimentally and analytically; and that the technique of scattered laser light be further developed and applied to measuring soot in POX exhaust.

## 2.0 Background

DARPA's interest in providing the US military with portable logistics fueled powerplants has led it to fund the development of diverse logistics fuel processors for fuel cell powerplants. Several of these fuel processors are based on steam reformers, others on autothermal reformers, and still others on POX reformers.

Three years ago ADL developed for DARPA, under subcontract to SOFCo, a JP-8 fuel processor based on a POX reformer. The success of this seven month long project was manifested by SOFCo's presentation of this fuel processor to the fuel cell community, for some time thereafter, as being of their own development.

During that SOFCo effort, it became apparent that reforming JP-8 at fuel equivalence ratios ( $\phi$ ) high enough to yield acceptable efficiencies inescapably resulted in the formation of soot.<sup>1</sup> This soot could befoul the POX reaction chamber if that chamber contained flow discontinuities, such as those resulting from less-than-tangential reactant inlet or from internally deployed thermocouples. But even with an aerodynamically clean POX reaction chamber, that soot could still befoul downstream components such as the desulfurizer. Consequently, that JP-8 fuel processor system employed a high temperature soot filter and an on-line filter cleaning system<sup>2</sup> downstream of the POX.

We had then, and have now, no reason to believe that diesel fuel would be any less soot-prone than JP-8.

Accordingly, when DARPA recently contracted with ADL<sup>3</sup> to provide a diesel fuel processor for a 250W PEMFC based on ADL's methanol or propane-fueled miniPOX, our agreed approach was to pre-process the diesel fuel such that it would yield considerably less, and ideally no, soot leaving the POX reaction chamber.

This approach was recognized as both critical and less than certain. The structure of the contract reflects this recognition by devoting Phase I (seven months) entirely to investigating the chemistry of pre-processing diesel fuel. Phase II efforts to build a prototype fuel processor system (in 24 months) would await the demonstrable establishment of this pre-processing chemistry.

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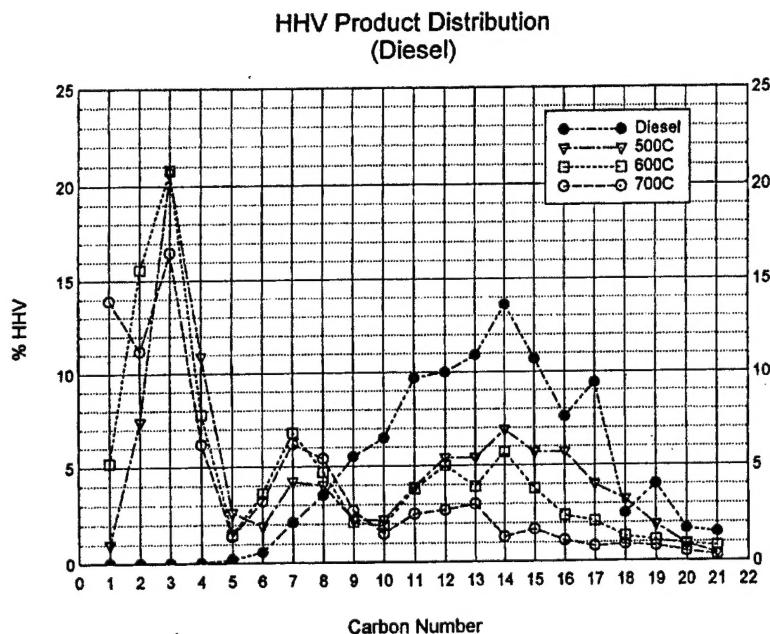
<sup>1</sup> Or, worse than soot, tar, if the operating temperature was too low

<sup>2</sup> The considerable bulk of that on-line filter cleaning system reflected its necessary creation in two weeks and the consequent lack of any experimental attempt to make it compact.

<sup>3</sup> Through the Army Research Office, Contract No. DAAG55-98-C-0042

### 3.0 Initial Technical Approach

Our initial technical approach was based on the apparent success that Aspen Systems had enjoyed with cracking diesel fuel, as exemplified by Figure 1.<sup>4</sup>

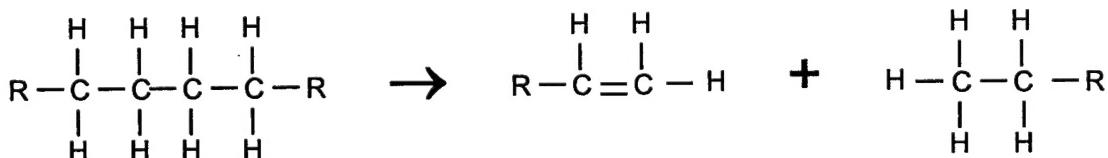


Cracking, and especially cracking at higher temperatures, reduces the energy value (that is, the concentration) of species with carbon numbers greater than 9.

Cracking, and especially cracking at higher temperatures, increases the energy value (that is, the concentration) of species with carbon numbers less than 8.

**Figure 1 – Cracking diesel fuel skews the carbon number distribution downward.**

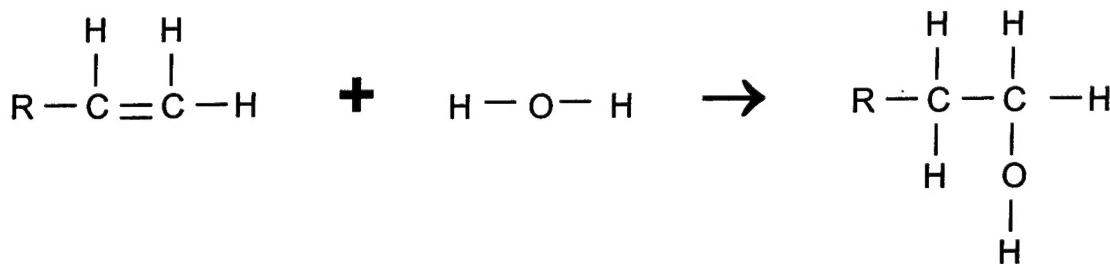
However, cracking diesel fuel does not merely skew the distribution of carbon numbers. By breaking apart even saturated hydrocarbons without adding hydrogen, cracking necessarily reduces their degree of saturation. For example, cracking alkanes necessarily results in the creation of olefins, per the process represented by Figure 2.



**Figure 2 – Cracking alkanes yields olefins.**

Recognizing olefins as soot precursors, we sought to hydrate these olefins into alcohols, which are not soot precursors, per the process represented by Figure 3.

<sup>4</sup> Jae Ryu, Alan Zhou and Dan Gobeille, "Hydrogen and Light Hydrocarbon Production from Logistic Fuels Via Catalytic Cracking," final progress report to the U.S. Army Research Office, contract no. DAAH04-95-C-0065, June 24, 1996.



**Figure 3 – Hydrating olefins yields alcohols.**

When we investigated the literature pertaining to olefin hydration, however, and when we performed chemical equilibrium calculations, we found that high pressures (>20 atm) were required. This is not surprising, for the product stream has fewer moles than the reactant stream and LeChâtelier's Principle applies.

Even at these high pressures, though, the percent conversion is low enough to require separation and recirculation of the hydrator product. Such operations are perhaps practical on a large stationary application, but they are clearly inappropriate for a small portable application.

Thus, after consulting with DARPA and ARO, we abandoned hydration as a practical means of pre-processing diesel fuel for small portable applications.

#### 4.0 The Nature of Diesel Fuel

Diesel fuel is much more than a collection of paraffins with boiling points ranging from 180°C to 360°C. It is a collection of paraffins, isoparaffins, aromatics, naphthenes and olefins with boiling points ranging from 180°C to 360°C. Many of these paraffins, isoparaffins, aromatics, naphthenes and olefins are alkylated, and some of those functional groups contain sulfur.

Figure 4 is a high-level description of the relevant reaction pathways for soot formation. A central role is played by highly dehydrogenated hydrocarbon fragments (such as dienes and acetylenic species) and polycyclic aromatic compounds (PACs) and polynuclear naphthenic compounds (PNCs).

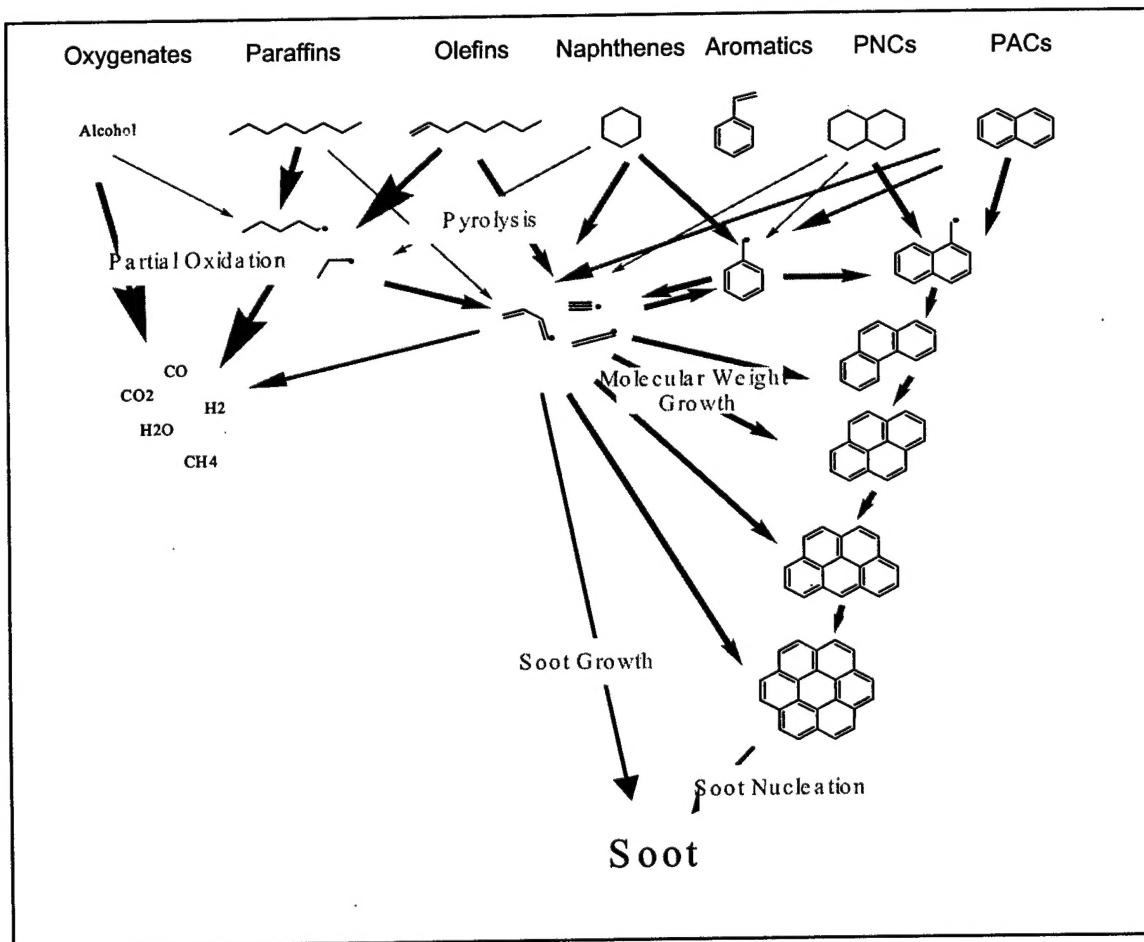


Figure 4 – Reaction Pathways for Soot Formation.

We modeled the reaction kinetics of some 1,102 elementary reactions between some 200 species to describe how the various components in diesel fuel can progress to the formation of PACs. As no chemical kinetic model could be found in the literature that describes all the relevant reaction classes for fuel rich combustion of diesel fuel, one was

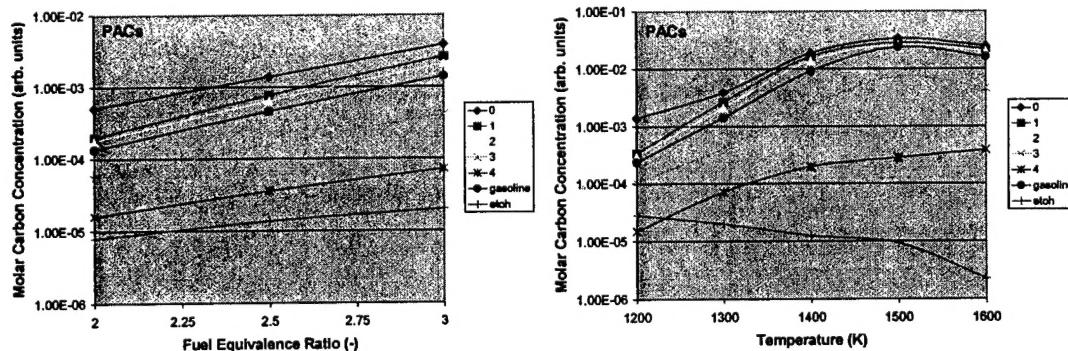
composed of reaction sets from a variety of sources. Two classes of reactions are not included: initial breakdown of naphthenes and PNCs, and the formation of solid soot. No mechanisms could be found for pyrolysis or oxidation of naphthenes so they had to be represented by a mixture of aromatics and olefins. The absence of soot formation from the model is not expected to significantly alter the trends predicted.

We used this model to predict the formation of PACs from the POX reaction of diesel fuel, of diesel fuel modified in various ways, and of gasoline and ethanol. The compositions assumed for each of these feedstocks is given in Table 1.

	<b>Diesel 0</b>	<b>Diesel 1</b>	<b>Diesel 2</b>	<b>Diesel 3</b>	<b>Diesel 4</b>	<b>Gasoline</b>	<b>Ethanol</b>
Composition in vol %	untreated	Diesel 0 PACs removed	Diesel 1 + 5% aromatics removed	Diesel 2 + all olefins / naphthenes cracked to ethylene	Diesel 3 + all ethylene hydrated to ethanol	untreated	untreated
Paraffin	40	40.4	42.6	21.7	21.7	40	-
Olefin	25	25.3	26.6	-	-	35	-
Ethyl- benzene	5	5.1	5.3	-	-	5	-
Toluene	29	29.3	25.5	13	13	20	-
Naphthalene	1	-	-	-	-	-	-
Ethylene	-	-	-	65.2	-	-	-
Ethanol	-	-	-	-	65.2	-	100

**Table 1 – Compositions of Feedstocks for Chemical Kinetics Modeling**

The results of this modeling, shown in Figure 5, suggest strongly that irrespective of  $\phi$  and operating temperature, the following conclusions obtain:



**Figure 5 – The concentration of PACs leaving the POX depends of the feedstock, the fuel equivalence ratio and the operating temperature.**

1. Diesel fuel from which all PACs and 5% of the MACs (mononuclear aromatic compounds) have been removed is just a bit more soot-prone than gasoline.
2. Diesel fuel in which, additionally, all olefins and naphthenes have been cracked to ethylene is considerably less soot-prone than gasoline.
3. Diesel fuel in which, additionally, all ethylene has been hydrated to ethanol is still less soot-prone than gasoline.

This suggests that removing PACs and some MACs from diesel fuel is worthwhile, as is cracking olefins and naphthenes. It also suggests that additionally hydrating, while effective, is superfluous.

## 5.0 Subsequent Technical Approach

We then considered, and evaluated experimentally, several approaches that involved cracking part or all of the diesel fuel. Of these, the one that showed the most promise involved the following steps:

1. Select, by fractionation, those species in diesel fuel that are most likely to cause soot; that is, those with a boiling point (hence carbon number) high enough to include the PACs. These are the species that remain as liquid in the fractionator and are removed as bottoms.
2. Pass the remaining species in diesel fuel (the overhead stream) through to the POX .
3. Crack/coke the selected species, the likely soot precursors, in a separate catalyst bed at high temperature.
4. Pass the lighter products of this cracking (hydrogen and functional groups) through to the POX.
5. Sequester the resulting coke in the catalyst bed until it become necessary to regenerate this catalyst.

This approach to dealing with soot precursors could be referred to as "Separate, Coke and Sequester." The experimental apparatus with which we evaluated this approach is shown in the figure to the right. A detailed description of this apparatus follows.

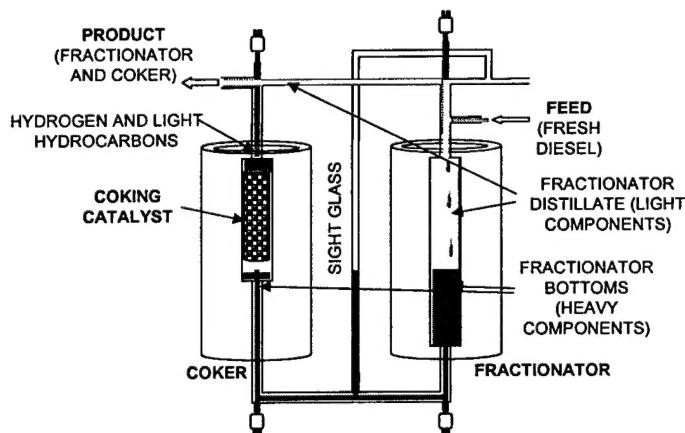


Figure 6 – Schematic Diagram of Fractionator/Coker

1. Diesel fuel is fed at roughly atmospheric pressure to the top of the fractionator, which is maintained at a temperature of 250-280°C in order to vaporize 75-95% of the diesel fuel. That vaporized portion, or light fraction, passes overhead.
2. The non-vaporized portion, or heavy fraction, of the diesel fuel leaves the fractionator as the bottoms stream and enters the bottom, non-catalytic, vaporizing section of the coker. This vaporizer is maintained at a temperature of 600°C, which is much hotter than is necessary to vaporize the rest of the diesel fuel. That hot vapor then passes up

through the packed bed of HY zeolite catalyst, in which bed temperature gradients are minimized by the 600°C vapor entering that bed.

3. This catalyst, which consists of -8 +16 mesh particles, is maintained at 500-750°C. This is hotter than is customary in refinery practice; refineries favor lower temperatures in catalytic crackers in order to minimize production of gaseous species and of coke. However, our application is best served by producing these lighter, gaseous species and by sequestering coke, so we operate at the highest possible temperatures consistent with catalyst life.
4. Flow from the fractionator bottoms to the coker is encouraged, and (we believe) flow stability enhanced, by putting both the fractionator overhead stream and the coker gaseous product stream into an eductor. The fractionator overhead stream serves as the motive stream, and the gaseous product stream as the suction stream. We operated this device both with and without this eductor.

## 5.1 Experimental Results

We operated the apparatus described above in three distinct fashions:

1. As shown in the above figure, with the fractionator overhead stream and the coker product stream mixed by the eductor and the eductor exhaust going to a condenser, so that we could use gas chromatographs to analyze
  - the non-condensable gaseous product species on-line, and
  - the condensable liquid product species subsequently.
2. With the fractionator overhead stream and the coker product stream separated and directed to individual condensers, so that we could use gas chromatographs to analyze
  - the non-condensable gaseous product species (assumed to be found entirely in the coker product stream) on-line, and both
  - the condensed fractionator overhead stream and
  - the condensable portion of the coker product stream subsequently.
3. As shown in the above figure, with the fractionator overhead stream and the coker product stream mixed by the eductor and the eductor exhaust stream directed to a small POX reactor. We analyzed a slipstream of the POX exhaust by gas chromatograph and we attempted to analyze the exhaust for soot using three separate techniques, as described later in this report.

### 5.1.1 Results of Mass Balance Analyses

By operating the fractionator and the coker separately, we were able to define the following four product streams, listed in order of increasing boiling point range:

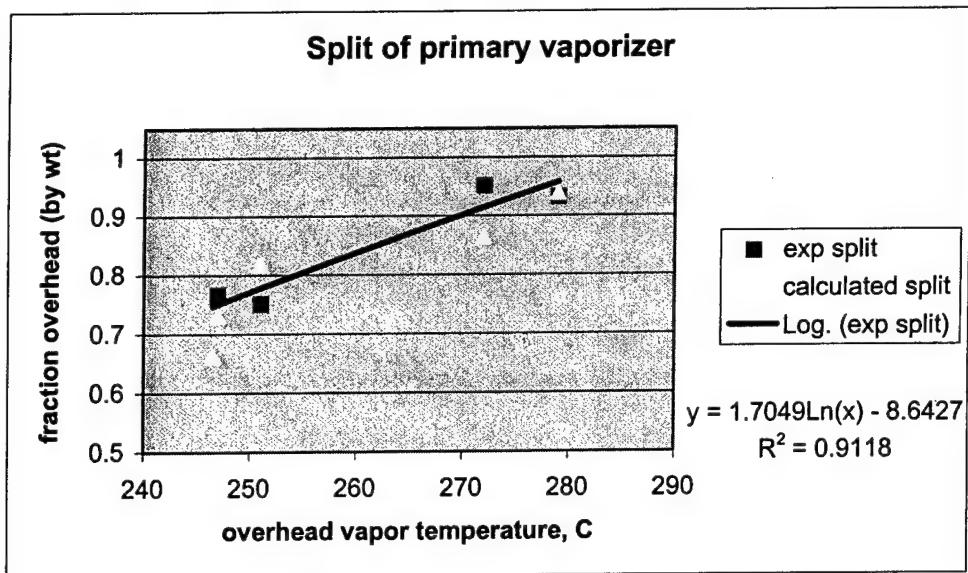
1. "Gas Make" – This is the gaseous, non-condensable product of the coker. It is made up primarily of hydrogen, methane and C2s.

2. "Overhead Liquid" – This is the fractionator distillate, which leaves the fractionator as vapor and is subsequently condensed for purposes of analysis.
3. "Coker Liquid" – This is the gaseous, but condensable, product of the coker that leaves the coker as vapor but is subsequently condensed for purposes of analysis. It is made up of three categories of species:
  - I. Heavy species that were not cracked in the coker.
  - II. Lighter species that resulted from cracking in the coker.
  - III. Heavier species that resulted from reactions of some of the products of cracking in the coker.
4. "Coke" – Actually, this is the "missing fraction" of the input diesel fuel, the part that did not turn up as either Gas Make, Overhead Liquid, or Coker Liquid. It is presumably made up of three categories of species:
  - I. Actual coke, a "black solid that is insoluble in any solvent and cannot be melted at any temperature"<sup>5</sup> which was presumably sequestered in the coker bed.
  - II. 'Quasi-coke,' or species which might volatilize and/or crack at higher temperatures but which did not do so at the operating temperature of the coker, which were also presumably sequestered in the coker.
  - III. Experimental error, presumably attributable to species that left the coker as vapor and were subsequently condensed for purposes of analysis, then were injected into the gas chromatograph but did not elute from the column.

Operating the fractionator by itself, we were able to determine that the mass fraction of the input diesel fuel that was vaporized (and that went to the overhead stream) was predictably determined by temperature, as shown by Figure 7.

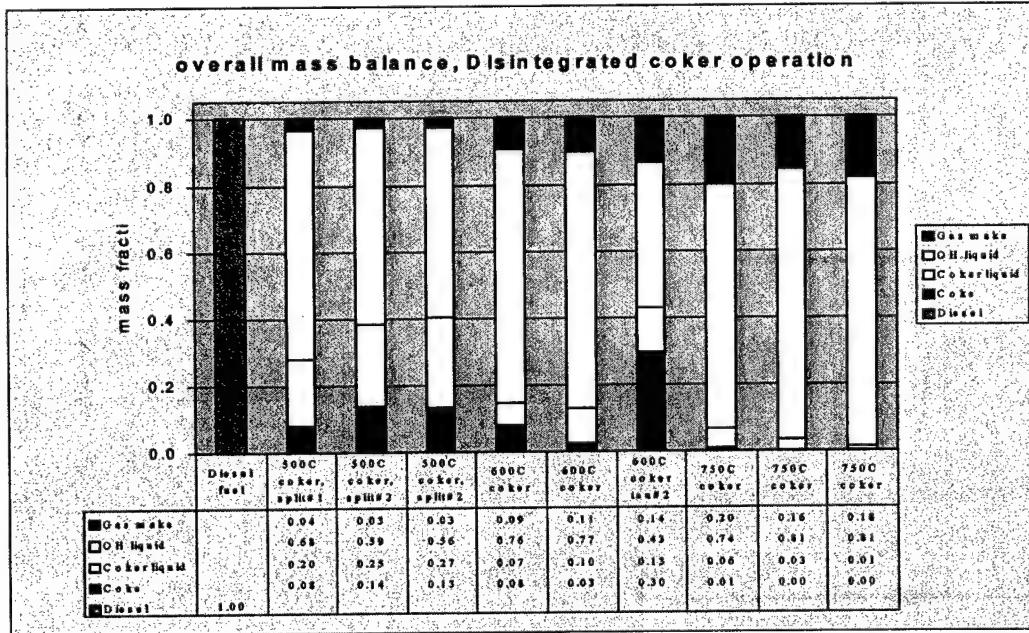
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<sup>5</sup> Irwin A. Wiehe, "The Chemistry of Coke Formation from Petroleum: A Tutorial," presented at the August 23-27 national meeting of the American Chemical Society, Boston, MA.



**Figure 7 – The overhead mass fraction is determined by the fractionator temperature.**

We were able to determine differences resulting from operating the coker at three different temperatures: 500°C, 600°C and 750°C. Temperatures higher than roughly 800°C were thought to be capable of harming the catalyst, so we avoided operating at such temperatures. These differences, which are apparent from Figure 8, are as follows:



**Figure 8 – Mass split depends strongly on coker temperature.**

1. Operating the coker at 750°C yields more Gas Make than at 600°C, and much more than at 500°C.
2. Operating the coker at 750°C may yield less Coker Liquid than at 600°C, and much less than at 500°C; coker liquid occurred in bursts, not all of which condensed.
3. Operating the coker at 750°C yields less Coke than at 600°C, and almost none at 500°C.

It is worth noting that refinery practice does not include operating catalytic crackers at such high temperatures, for in refineries the gaseous products that are thus maximized are considered to be products of lower value than the heavier, condensable liquid products.

### 5.1.2 Results of Gas Chromatograph Analyses

When we chemically analyzed the Overhead Liquid, the results were discouraging. As Figure 9 shows, the Overhead Liquid appears to have roughly the same distribution of weight fractions as the diesel fuel.

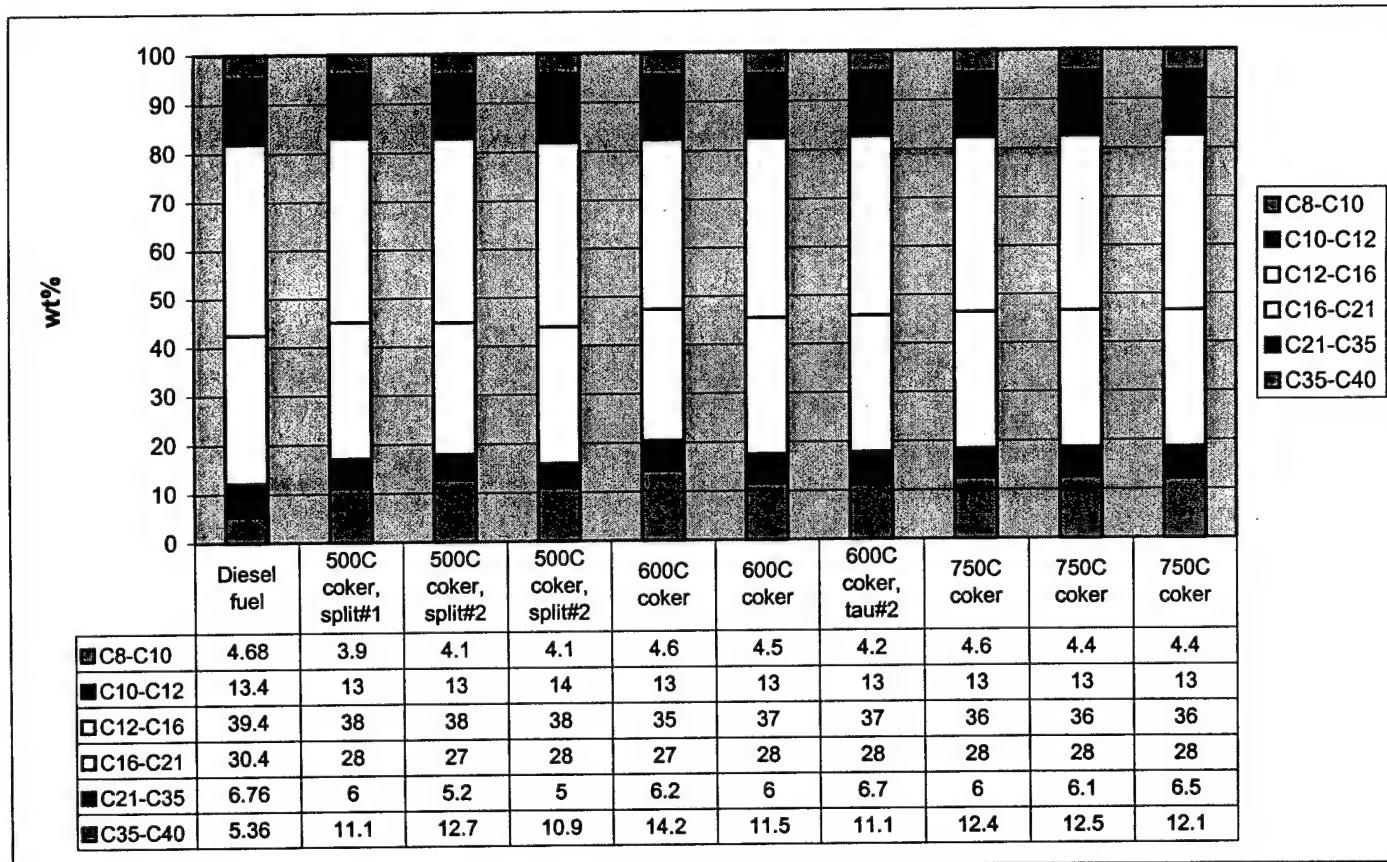


Figure 9 – The Overhead Liquid is not very different from diesel fuel.

This observation confirms what we should have suspected, namely that the separation afforded by a single plate still is not nearly as effective as would be afforded by a distillation column. After all, a distillation column is required to separate diesel fuel from gasoline and kerosene (technically, to separate straight run gas-oil from straight run gasoline and kerosene). How could it require any less than a distillation column to separate one portion of diesel fuel from another?

Using a distillation column to separate the lighter fractions of diesel fuel from the heavier fraction of diesel fuel is perhaps possible for larger, stationary applications. A distillation column cannot be considered practical for a small, portable application.

When we chemically analyzed the Gas Make and the Coker Liquid as well, the results also suggested that the fractionator was ineffective. As can be seen from Figure 10, the Gas Make appears to be the result of cracking all weight fractions, not just the heavier fractions.

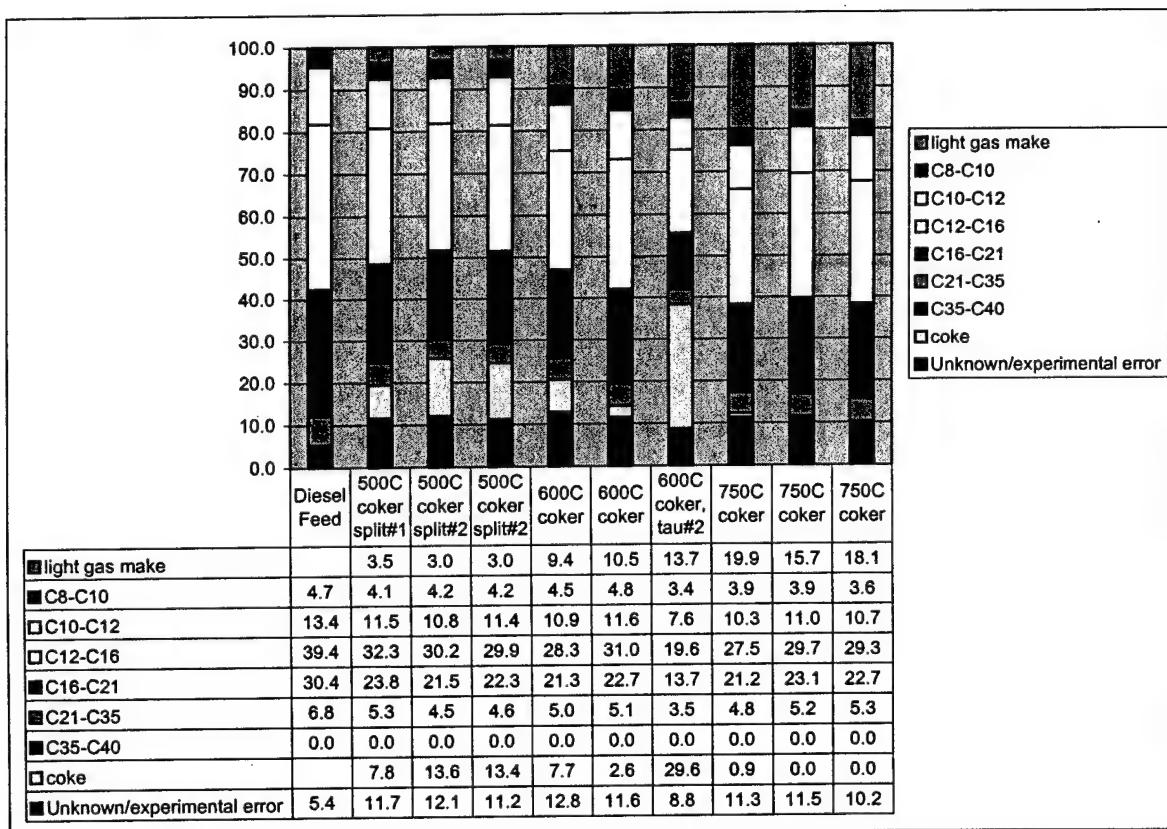


Figure 10 – The Gas Make appears to come from all fractions in diesel fuel.

### **5.1.3 Soot Analyses**

We were unable to make any meaningful measurements of soot in the POX exhaust stream. This was true both when the POX was fueled with untreated (that is, merely vaporized) diesel fuel, and when it was fueled with the product stream from the fractionator/coker. Neither were we able to visually detect much soot in the POX exhaust.

In all cases, the POX reformer was oriented vertically, so that its input fuel/air entered the well stirred zone tangentially and horizontally at the bottom, and so that it exhausted vertically upward from the plug flow zone into the hood.

Let us first address the limitations of the three experimental techniques we employed.

1. Laser scattering
2. Smokemeter
3. Low temperature filter

Then let us address why there may have been so little soot to observe.

#### **5.1.3.1. Laser Scattering Technique**

We directed the beam from a 250 mW Melles Griot model 05-LHP-991 632.8nm helium-neon laser horizontally through the exhaust stream at an elevation of several millimeters above the reformer's exhaust tube. We deployed an International Light model SEE015 photodiode detector so that it would receive any laser light that was scattered roughly 55 degrees to the right, in the horizontal plane. Between the scattered light source (that is, the POX exhaust stream) and the detector we deployed a telescope to concentrate scattered light onto the detector, as well as a Melles Griot model 03-FIL-008 632.8nm band-pass interference filter (632 +/- 0.5 nm) to render the detector selectively sensitive to light of frequency roughly equal to that of the laser.

The variation in the detector readings was such that we were unable to distinguish a signal above the noise. This inability suggests either too low a signal, or too high a noise level, or both. Perhaps we could have distinguished a signal had we used a more powerful laser and/or a chopper. However, neither was available to us and space limitations might have precluded their use anyway.

#### **5.1.3.2 Smoke Meter Technique**

We then drew much of the POX exhaust through a stainless steel tube into an AVL model 415 variable sampling smoke meter, using the sample pump that is part of this instrument. This instrument is used in ADL's engine test lab to measure soot in diesel engine exhaust. It works by drawing a measured exhaust sample through a piece of filter paper for a set period of time and then measuring the absorption of light by that filter paper.

This techniques suffered primarily from the excess flow required by the smoke meter, which distorted the air and fuel flow rates input to the POX reformer. We made numerous attempts to change the flow rate to the instrument, but success would have required at least more assistance than we were able to obtain from the manufacturer.

#### **5.1.3.3 Low Temperature Filter Technique**

We attempted to cool a slipstream of the POX exhaust and then pass it through a low temperature filter element. The intent was to weigh the filter element before and after, but we encountered difficulties in dismantling the filter housing after the first experimental run.

We then abandoned this technique, recognizing that it shared with the smoke meter technique the following drawback.

#### **5.1.3.4 Problem with Low Temperature Soot Measuring Instruments**

One important observation made during our earlier JP-8 reformer effort for SOFCo is that high operating temperatures are required to convert all of the soot precursors into soot. Table 2<sup>6</sup> suggests that an operating temperature near 2100°F (1150°C) is

	Run No. C-66	Run No. C-58
Firing rate	9.0 lb/hr	9.5 lb/hr
Fuel equivalence ratio	3.5	3.6
Steam/carbon ratio	1.2	0.7
Water fraction	39%	0%
Reaction temperature	1700°F	2100°F
Monocyclic aromatic compounds + C <sub>7</sub> thru C <sub>10</sub>	0.12 vol %	0.01 vol %
Polycyclic aromatic compounds + C <sub>11</sub> and up	0.01 vol %	0.00 vol %
Soot	0.09 vol %	0.14 vol %

**Table 2 – The operating temperature determines if tar and/or soot will form.**

required to eliminate virtually all of the heavy hydrocarbons and to convert at least some of them to soot. If the POX is operated at lower temperatures, then these tar producers/soot precursors will exist in the POX exhaust stream. Unless the sample line and the filter housing are both heated to prevent the condensation of these species as tar, the filter can only trap those soot particles that were

- (a) produced in the POX, and which
- (b) escaped depositing in the sample line on the sticky tar layer.

Neither the smoke meter technique nor the low temperature filter technique included a heated sample line. Neither the low temperature filter nor the smoke meter were

<sup>6</sup> "JP-8 Reformer, Final Report," report to SOFCo, Reference 57070, March 28, 1996, p. 14.

maintained at temperatures high enough to prevent the condensation of tar. Consequently, neither technique as practiced could be expected to provide a meaningful measurement of soot in the POX exhaust.

The laser scattering technique was expected to detect soot and only soot, for yet-to-be condensed tar would not scatter the laser beam.

## 5.2 Achieving the Required POX Operating Temperature

Let us consider how possible, and how practical, it might be to build a small POX reactor that can operate at the temperatures required to reform diesel fuel, even pre-processed diesel fuel; especially, to reform it without producing tar. This requires us to address two separate questions:

1. What temperatures are required to reform diesel fuel?
2. How small can a POX reactor be and still achieve any given operating temperature?

The results presented in the above table suggest that for JP-8 to yield soot, rather than tar, requires an operating temperature on the order of 1150°C (2100°F). It stands to reason, though we cannot confirm, that for diesel fuel (with its higher content of PNCs and PACs) to yield soot rather than tar would require an even higher temperature. Again, it stands to reason, though we cannot confirm, that not as high a temperature would be required to yield soot rather than tar from diesel fuel that has been pre-processed to remove some or all of the PNCs and PACs.

The temperature of a partial oxidation reaction is determined by the following four energies:

1. The chemical energy released by the combustion reactions
2. The sensible (and perhaps latent) energy required to raise all reactants and diluents to that temperature
3. The chemical energy required by the reforming reactions
4. The energy transferred from the reaction zone by radiation, conduction and convection

The first three of these energies are proportional to the volume<sup>7</sup> of the combustion zone, and the fourth of these energies is proportional to the surface area of the combustion zone. Thus, a POX reactor that is geometrically similar to another with twice the linear dimension can expect

- to generate 1/8 as much chemical energy by combustion, and

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<sup>7</sup> Strictly speaking, they are proportional to the reactant throughput; however, for a given residence time the reactant throughput is proportional to volume.

- to require 1/8 as much sensible energy to reach a given combustion temperature, given the same ratio of reactants to diluents, and
- to require 1/8 as much chemical energy to reform the un-combusted fuel, but
- to transfer  $\frac{1}{4}$  as much heat from the reaction zone, given a constant overall heat transfer coefficient and a given combustion temperature.

Other things being equal, the smaller reactor must operate at a lower combustion temperature, so that energy generated by the reaction can again balance the sensible energy required, the chemical energy required and the heat transferred.

To maintain a given combustion temperature with the smaller POX reactor, it is necessary either

- to decrease the sensible heat absorbed by diluents, as by decreasing the steam:carbon ratio; or
- to decrease the chemical energy required to reform the un-combusted fuel, as by decreasing the fuel equivalence ratio (lower  $\phi$ , less un-combusted fuel to reform); or
- to decrease the overall heat transfer coefficient from the POX reactor, as by adding insulation; or
- to perform some combination of these.

However, each of these techniques has its limits:

1. The steam:carbon ratio can only be reduced to zero. Also, any reduction in the steam:carbon ratio may increase the formation of soot.
2. The fuel equivalence ratio can be reduced, but fuel cell system efficiency will be impacted in the following two ways:
  - I. The cold gas efficiency of the reformer, defined as the ratio of the chemical energy in the reformate to the chemical energy in the fuel, decreases with decreasing  $\phi$  per Figure 11:

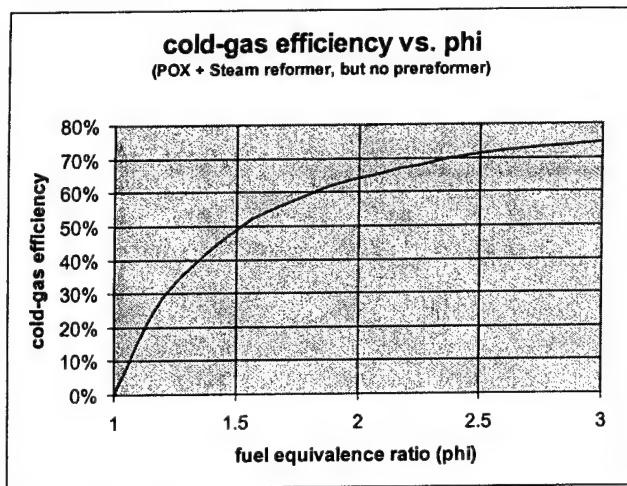


Figure 11 – Cold Gas Efficiency vs. Fuel Equivalence Ratio

II. As the inlet hydrogen concentration is decreased, that hydrogen which is utilized by the fuel cell is utilized less efficiently, per Figure 12<sup>8</sup>:

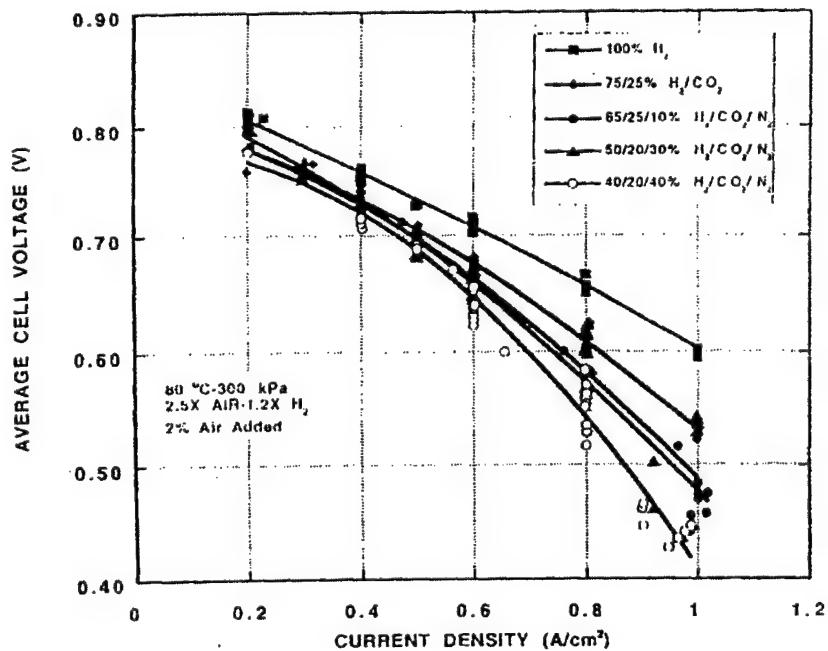


Figure 12 – Polarization curves degrade substantially with decreasing [H<sub>2</sub>].

<sup>8</sup> M. Inbody, J. Tafoya, J. Hedstrom, N. Vanderborgh, "Fuel Cell Stack Testing at Los Alamos National Laboratory," *DOE Fuel Cells for Transportation Exploratory R&D Program*, Washington, D.C.: Los Alamos National Laboratory; taken from C. Thomas, B. James, F. Lomax, "Market Penetration Scenarios for Fuel Cell Vehicles, presented at the 8<sup>th</sup> Annual U.S. Hydrogen Meeting, 11-13 March 1997, Alexandria, VA.

These results may reflect the decreased anode hydrogen utilization that is to be expected when the inlet concentration of hydrogen is decreased. Alternatively, decreased anode hydrogen utilization could be a third negative impact of low fuel equivalence ratio. To determine which explanation applies would require knowing if the inefficiency implied by lower polarization curves was accompanied by additional heat lost to the fuel cell's cooling stream.

3. The overall heat transfer coefficient of the POX reactor can be decreased by insulating it better. However, certain realities must be observed:

- I. Insulating the outside of the stainless steel structure that comprises the POX reactor has its limitations. For example, were a vacuum jacket to be constructed around this stainless steel structure (as has been suggested), the overall heat transfer coefficient would indeed be decreased, but the temperature of the inside surface could easily be raised above the temperature at which stainless steel, even SS310, melts.
- II. Insulating the inside of the stainless steel structure that comprises the POX reactor would be effective. However, that inside insulation must be quite thick for a small reactor, thicker than geometric similarity would provide. Figure 13 demonstrates this effect.

## FULL SIZE POX REACTOR      HALF SIZE POX REACTORS

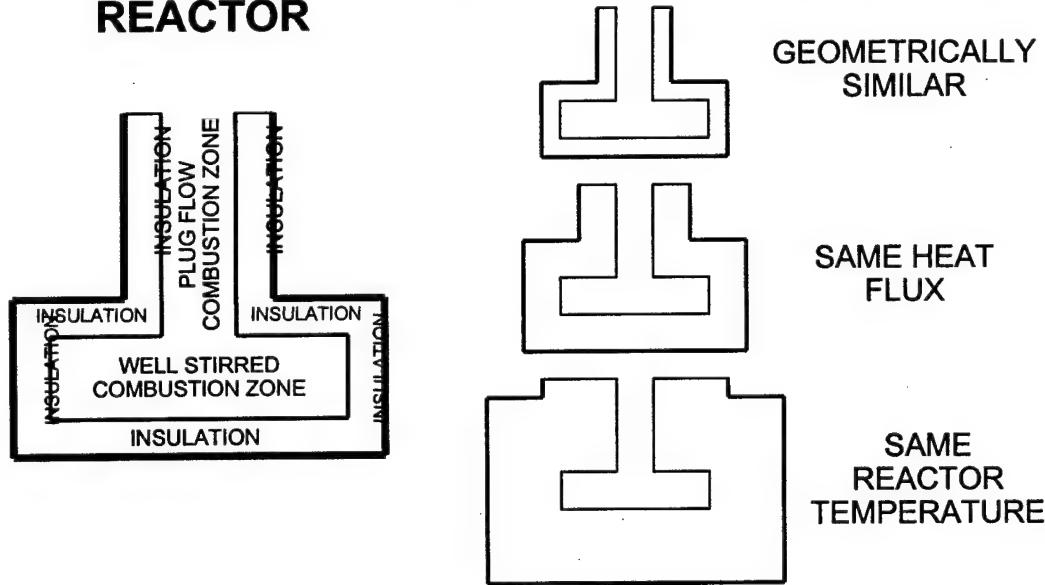


Figure 13 – As POX reactors get smaller, insulation thickness dominates.

- A half-size reactor with geometrically similar (that is, half-thickness) insulation would permit twice the heat flux if the combustion temperature were the same. Of

course, the combustion temperature cannot be the same, due both to the doubled heat flux and to the doubled ratio of surface area to volume.

- A half-size reactor with same-thickness insulation would permit the same heat flux if the combustion temperature were the same. Of course, the combustion temperature cannot be the same, due to the doubled ratio of surface area to volume.
- A half-size reactor with twice the thickness of insulation will have half the heat flux. This is required because of the doubled ratio of surface area to volume, in order to permit the same combustion temperature.

Diminishing returns accrue from miniaturizing POX reactors past a certain point. In the above figure, the only half-size reactor that is capable of maintaining the same combustion temperature as the full-size reactor turns out to be, once the necessary insulation is applied, almost as bulky and as heavy as the full-size reactor.

Were the linear dimension of the POX reactor to be halved again, the thickness of the insulation layer would have to be doubled again. The resulting reactor-plus-insulation assembly would be even larger than the reactor shown in the lower right hand corner of the above figure.

It should be recognized that the foregoing analysis applies to a POX reactor that operates at a single design point. If it is desired instead that a POX reactor be capable of turndown, then it must be capable of achieving a sufficiently high operating temperature at its minimum desired capacity.

## 6.0 Conclusions

Even disappointing results yield knowledge. From these results we conclude the following:

1. Hydration of olefins requires high pressures, plus separation and recirculation of the product stream, and is impractical for a small portable system.
2. Achieving the following results by pre-processing would render diesel fuel only as prone to soot formation as gasoline:
  - Removal of all polycyclic aromatic compounds, plus
  - Removal of some of the monocyclic aromatic compounds, plus
  - Cracking of some of the olefins and naphthenes to ethylene.
3. Using a single plate still as a fractionator does not afford the degree of separation necessary to permit the success of a scheme to crack and coke only the heavier species within diesel fuel.
4. Using a distillation column as a fractionator could afford the degree of separation necessary to permit the success of a scheme to crack and coke only the heavier species within diesel fuel, but is impractical for a small portable system.
5. The coker yielded three products. In addition to the desired two products, Gas Make and Coke, it yielded an unwanted product, Coker Liquid. Coker Liquid can be minimized by operating the coker at 750°C, and could be separated from Gas Make by condensation, but separations would introduce level of complexity inappropriate to a small, portable application.
6. The degree to which diesel fuel has been rendered, though pre-processing, less likely to produce soot and tar can best be measured by feeding it to a POX reactor operating hot enough to produce soot instead of tar.
7. Measurement of soot in the POX exhaust cannot be accomplished reliably if that exhaust stream is allowed to cool to the point that tar can condense, for soot will likely be trapped in that tar layer.
8. There is a minimum practical size for POX reactors, below which size it is impossible to maintain the desired operating temperature without unduly compromising efficiency by running with too low a fuel equivalence ratio.
9. A POX reactor that must operate over a range of firing rates must be large enough that it can meet that desired operating temperature at its minimum firing rate.

## 7.0 Recommendations

Based on the above conclusions, we make the following recommendations:

1. That the concept of pre-processing diesel fuel be further explored in the context of larger, stationary systems; such applications can afford the complexity associated with distillation columns and alternating, regenerable beds of coking catalyst.
2. That the minimum practical size of POX reactors be determined both experimentally and analytically, using perhaps two sizes of ceramic-lined POX reactors and the laws of scaling as they apply to conduction heat transfer.
3. That the technique of scattered laser light be further developed and applied to measuring soot in POX exhaust; without such a technique, it is virtually impossible to demonstrate the extent to which any fuel pre-processing technique is successful.

# REPORT DOCUMENTATION PAGE

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13. ABSTRACT (Maximum 200 words)

We built and tested a device intended to render diesel fuel acceptable to a 250W portable POX-based fuel processor. The premise, established by chemical kinetics analysis, was that diesel fuel is reformable by POX once its polycyclic aromatic compounds are removed and its naphthenes and olefins cracked. Our device utilized a single plate still to separate those species already light enough to reform from those species heavy enough to require further treatment. Further treatment consisted of a cracking catalyst intended to crack heavy species partly into reformable vapors and partly into coke to be sequestered within the catalyst bed. We concluded that this technique requires better separation than is possible with a single plate still.

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